



PCT/AU 99/01101
09/857611

REC'D	08 FEB 2000
WIPO	PCT

AV 99/1101
4

PRIORITY DOCUMENT

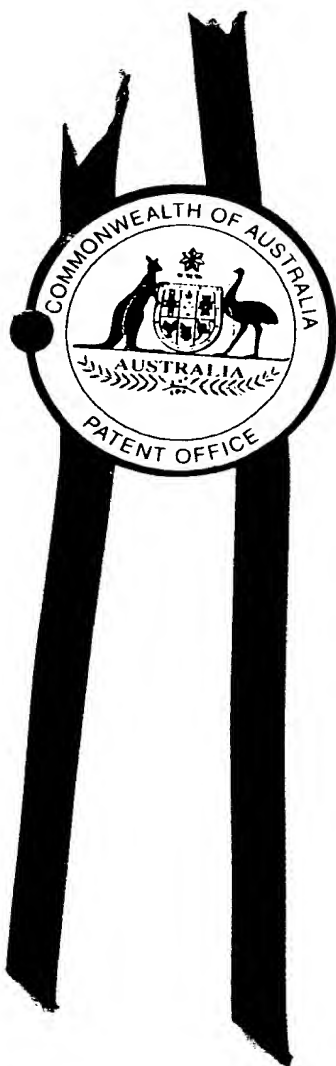
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Patent Office
Canberra

I, KIM MARSHALL, MANAGER PATENT OPERATIONS hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PP 7696 for a patent by FOOD & PACKAGING CENTRE MANAGEMENT LIMITED filed on 14 December 1998.

WITNESS my hand this
Twelfth day of November 1999

KIM MARSHALL
MANAGER PATENT OPERATIONS



AUSTRALIA
Patents Act 1990

PROVISIONAL SPECIFICATION

PP **filed 14th December 1998**

Invention Title : **Biodegradable Film**

Applicant: **Food & Packaging Centre Management Limited**
[A C N 070 675 464]

Inventors: Gregor Christie
Long Yu
Steve Coombs

The invention is described in the following statement:

Biodegradable Film

This invention relates to improvements in biodegradable polymeric products particularly starch based polymers for use in flexible films.

5

Background to the invention

There is an increasing demand for many plastic products used in packaging to be bio degradable. Trays in biscuit and chocolate packages are one example.

Starch films have been proposed as biodegradable alternatives for some time.

10 USA patent 3949145 proposed a starch/polyvinyl alcohol/glycerol composition for use as a biodegradable agricultural mulch sheet.

Difficulties have been encountered in producing starch based polymers particularly by hot melt extrusion. The processing of thermoplastic starches is more complex than for conventional thermoplastics because the processing involves
15 gelatinisation, melting, volume expansion, molecular degradation and other physiochemical changes typical of starches. The molecular structure of the starch is adversely affected by the shear stresses and temperature conditions needed to plasticise the starch and pass it through the extrusion die. For most products foaming has to be avoided and this generally requires attention because of the
20 water content of the starch. Foaming has been avoided by degassing the melt prior to exiting the die as suggested in USA patents 5314754 and 5316578. The latter patent also avoids adding water to the starch. As explained in USA patent 5569692 by not drying starch and avoiding the addition of water the starch can be processed at temperatures between 120°C and 170 °C because the water bound
25 to the starch does not generate a vapour pressure such as to require high pressures.

Another approach to improving the melt processability of starch is to provide an additive as in USA patent 5362777 which reduces the melting point of the starch. The additive is selected from dimethyl sulfoxide, a selection of polyols and amino
30 or amide compounds.

In order to produce starch polymers for particular applications they have been blended with a range of other polymers. Biodegradable blown films are disclosed in USA patent 5322866 which blends raw starch, polyvinyl alcohol and talc with glycerol and water. USA patent 5449708 discloses compositions of starch ethylene

acrylic acid and a salt of stearic acid plus a glycerol based lubricant. Flexible and clear transparent sheets are disclosed in USA patent 5374304. These are composed of a high amylose starch and a glycerol plasticizer. The use of starch in conjunction with high amylose or modified starches has also been proposed. USA
 5 patents 5314754, and 5316578 both suggest the use of modified starches including hydroxypropyl substituted starches. Hydroxypropylation reportedly increases elongation at break and burst strength and improved resilience in the polymers. Although the efficacy of these special and modified starches is recognised their cost inhibits the commercial acceptability of the products made
 10 from them.

It is an object of this invention to provide a biodegradable polymer which can be processed and blown or drawn into flexible films without difficulty and have acceptable properties for its intended uses.

15 **Brief Description of the Invention**

To this end the present invention provides a thermoformable biodegradable film forming polymer having the composition

- a) from 10 to 50% by weight of a starch modified by reaction with an hydroxyalkyl C_{2-6} group or an anhydride of a dicarboxylic acid
- 20 b) from 0 to 74.9% of starch
- c) from 5 to 12% by weight of a water soluble polymer selected from polyvinylacetate, polyvinyl alcohol and copolymers of ethylene and vinylalcohol which have a melting point compatible with the molten state of the starch components
- 25 d) from 10 to 25% by weight of a polyol plasticiser
- e) from 0.1 to 1.5 % by weight of a C_{12-22} fatty acid or salt and
- f) from 0 to 20 % by weight of added water.

The compositions of as defined are easier to process as they can be extruded and
 30 drawn or blown in film form without foaming for use as biodegradable packaging. Usually the need to vent the extruder to remove water prior to the mix exiting the extrusion die is not needed with this formulation.

The upper limit to the content of the modified starch is determined by its cost. This component contributes structural benefits to the resulting material. A preferred

component is hydroxypropylated amylose. Other substituents can be hydroxy ethyl or hydroxybutyl to form hydroxyether substitutions, or anhydrides such as maleic phthalic or octenyl succinic anhydride can be used to produce ester derivatives. The degree of substitution[the average number of hydroxyl groups in a unit that are substituted] is preferably 0.05 to 2. The preferred starch is a high amylose maize starch. A preferred component is a hydroxypropylated high amylose starch A939 marketed by Goodman Fielder. A preferred concentration range to meet cost parameters is 12 to 24 %

The other starch component is any commercially available starch. This may be derived from wheat, maize, potato, rice, oat, arrowroot, and pea sources.

Generally the water content is about 10 to 15 %. A preferred concentration range for starch is 50 to 70.6%

The polymer component c) of the composition is preferably compatible with starch, water soluble, biodegradable and has a low melting point compatible with the processing temperatures for starch. Polyvinyl alcohol is the preferred polymer but polymers of ethylene-vinyl alcohol, ethylene vinyl acetate or blends with polyvinyl alcohol may be used. A preferred concentration range for sheet material is 7 to 9%.

The preferred plasticiser is glycerol although ethylene glycol and diethylene glycol are also suitable as is sorbitol. Cost and food contact are important issues in choosing the appropriate plasticizer. Higher concentrations of the plasticiser render the resulting material more flexible. A preferred concentration range is 10 to 16%.

The fatty acid or fatty acid salt component is preferably present in concentrations of 0.6 to 1%. Stearic acid is the preferred component. Sodium and potassium salts of stearic acid can also be used. Again cost can be a factor in the choice of this component but Lauric, myristic, palmitic, linoleic and behenic acids are all suitable. It is found that the acid tends to accumulate near to the surface of the composition as it is extruded.

Water is added to the composition if the water content of the starch components is insufficient for the needs of processability.

Detailed description of the invention

Processing conditions depend on the formulations and the desired properties of the product to be produced. The materials need to be heated above 140 °C in the

extruder to fully gelatinise the starches. The die temperature needs to be controlled below 110 °C to avoid foaming.

The preferred method of carrying out this invention involves mixing the starch, modified starch, vinylalcohol polymer lubricant and fatty acid components into a free flowing powder. The premixing can be carried out in any conventional mixer. The powder is then introduced into a screw extruder and subjected to an elevated temperature by the shearing action of the screw and the application of external heat to the barrel. The temperature is raised to a maximum in the range of 130°C to 160 °C. Any liquid components including additional water are introduced during this initial phase. The melt that is formed is then propelled toward the die and in moving forward the temperature is reduced to a value in the range of 85 °C to 105°C.

A typical extrusion for rigid products has the following parameters:

Temperature profile °C : 60, 70, 90, 110, 130, 145, 130, 120, 110

Screw Speed 120 rpm

Die Pressure 1400 psi

Flexible film can be formed by simply extruding from a sheet forming die and the increasing the speed of a take off roller to achieve the reduced thickness needed for flexible film. Cooling of the film between the die and the roller is usually needed to ensure that the film does not adhere to the roller. De-humidified air to cool the film also assists in removing excess moisture from the film surface. If the film is formed by the blown tube method dehumidified air is used to blow the film as it exits the die. Talc may also be entrained in the air stream to reduce blocking of the film.

Formulations of starch based mixes in accordance with the invention were extruded into sheet form. The formulations and the initial observations of the sheet performance are given in the table 1.

TABLE 1

Example	A939 [hydroxy propylated amylose]	Wheat Starch	PVOH	Glycerol	Stearic Acid	Remarks
1	37.46	37.46	8.1	14.29	0.84	Includes 4.02% talc no foam, fairly flexible, very strong
2	33.51	33.51	7.46	21.05	0.75	Includes 3.72% CaCO ₃ No foam, flexible, weak
3	34.42	34.42	7.66	18.92	0.77	Includes 3.81% CaCO ₃ slight foam, flexible, strong
4	35.38	35.38	7.88	16.67	0.79	Includes 3.92% CaCO ₃ slight foam, flexible, strong
5	37.34	37.34	7.87	16.67	0.78	no foam, flexible, strong
6	38.41	38.41	8.08	14.29	0.81	no foam, flexible, strong
7	39.71	39.71	8.03	11.76	0.79	no foam, flexible, very strong
8	38.03	38.03	7.69	11.27	0.76	Includes 4.23% water no foam, flexible, fairly strong
9	81	0	8	10.2	0.8	
10	65	16	8	10.2	0.8	
11	57	24	8	10.2	0.8	
12	24	57	8	10.2	0.8	
13	16	65	8	10.2	0.8	
14	0	81	8	10.2	0.8	

Examples 15 - 22

- 5 The effect of stearic acid content on the composition was tested using a formulation of :

	Wheat starch	36%
	Modified Amylose A939	36%
	Polyvinyl alcohol	8%
10	Glycerol	10%
	Water	10%

The mixture was processed at a feed rate of 1.5 a screw speed of 100 rpm and the temperature profile was 70, 90, 100, 130, 140, 140, 130, 115, 110, 110, 110[die]

Sample	Stearic acid content [%]	Torque [%]	Mass [g/min]	Quality of Sheet [observation]
15	0.0	57	101	Rough surface
16	0.4	51	100	Nice sheet
17	0.8	44	106	Nice sheet
18	1.2	39	114	Nice sheet
19	2	38	106	Sheet with some holes
20	3	38	106	Sheet with holes
21	4	35	101	Sheet with a lot of holes
22	5	34	102	Sheet with a lot of holes

The results show that torque is decreased with increase in stearic acid content. Output mass peaks at a stearic acid content of 1.2 g. the preferred range of stearic acid is 0.4 to 1.5 %.

5

From the above it can be seen that the present invention provides a biodegradable starch polymer film that is comparable in price and performance characteristics to conventional non-biodegradable polymer films. Consequently packaging of products such as bread, in flexible packaging, can be just as presentable and attractive with the added benefit of being environmentally friendly.

10

15

20

CLAIMS

1. A film forming biodegradable polymer having the composition
 - a) from 10 to 50% by weight of a starch modified by reaction with an hydroxyalkyl C₂₋₆ group or an anhydride of a dicarboxylic acid
 - 5 b) from 0 to 74.9% of starch
 - c) from 5 to 12% by weight of a water soluble polymer selected from polyvinylacetate, polyvinyl alcohol and copolymers of ethylene and vinylalcohol which have a melting point compatible with the molten state of the starch components
 - 10 d) from 10 to 25% by weight of a polyol plasticiser
 - e) from 0.1 to 1.5 % by weight of a C₁₂₋₂₂ fatty acid or salt and
 - f) from 0 to 20 % by weight of added water.
2. A composition as claimed in claim 1 wherein component e) is stearic acid.
- 15 3. A composition as claimed in claim 1 or claim 2 wherein component c) is a polyvinyl alcohol component d) is glycerol.

ABSTRACT

A film forming, biodegradable polymer is disclosed having the composition

a) from 10 to 50% by weight of an amylose starch modified by reaction with an

5 hydroxyalkyl C_{2-6} group or an anhydride of a dicarboxylic acid, preferably
hydroxy propylated high amylose starch

b) from 0 to 74.9% of starch

c) from 5 to 12% by weight of a water soluble polymer selected from

10 polyvinylacetate, polyvinyl alcohol and copolymers of ethylene and vinylalcohol
which have a melting point compatible with the molten state of the starch
components

d) from 10 to 25% by weight of a polyol plasticiser, preferably glycerol

e) from 0.1 to 1.5 % by weight of a C_{12-22} fatty acid or salt, preferably stearic acid
and 0 to 20 % added water

15 The polymers are suitable as biodegradable film for use in packaging.